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DETERMINATION OF THE NATURE AND CONTENT OF ANTIOXIDANT AND ANTIOXIDANT SYNERGIST IN PE AND XLPE USED IN CABLES

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ABSTRACT

It is shown that PE and XLPE resins used for cable applications contain an antioxidant synergist in addition to an antioxidant. Their nature and content have been determined by a combination of UV and FTIR spectroscopy and neutron activation analysis measurements. The results thus obtained suggest that part of the antioxidant compound is grafted to polymer chains during crosslinking.

Keywords

Polyethylene, Crosslinked polyethylene, Antioxidant, Synergist, Oxidation

INTRODUCTION

High-voltage underground cables are being insulated more and more with extruded polyethylene (PE) and crosslinked PE (XLPE). These materials contain antioxidant to protect them against thermal degradation. Recently, antioxidant synergists have been added to PE and XLPE resins to interrupt the degradative cycle associated with the decomposition of hydroperoxides and also to limit the consumption of antioxidant during cable extrusion.[1,2] In fact, little is known concerning the real efficiency of this additive since most resin manufacturers do not reveal its presence and also because they keep its formulation and content proprietary. Nevertheless, it is possible to determine the nature and content of the antioxidant compound in PE by IR and UV spectroscopy[3-6] and also by HPLC.[6-7] However, the two latter techniques are of limited use with XLPE because the crosslinking by-products strongly absorb UV light and also because antioxidant cannot be extracted from XLPE, possibly due to grafting.[7,8] FTIR spectroscopy can identify most antioxidants, but carbonyl groups generated during oxidation can interfere with ester groups of the additive, making its identification difficult in aged PE and XLPE. There is therefore no single reliable technique that enable us to evaluate the nature and content of antioxidant and antioxidant synergist in XLPE.

Since many antioxidants and synergists contain sulfur, it has already been proposed to evaluate the amount of antioxidant from the sulfur content.[1,8] One objective of this paper is to show that, indeed, the concentration of the antioxidant compound in XLPE can be accurately determined from the sulfur-content measurement. For that purpose, we have performed neutron activation analysis (NAA) measurements on PE and XLPE samples. In order to determine the nature of the antioxidant synergist, Fourier Transform Infra Red (FTIR) and UV spectroscopy measurements were also performed. It is shown that the best way to identify and quantify antioxidant and antioxidant synergist in XLPE is to combine UV and FTIR spectroscopy with NAA measurements. The influence of crosslinking on the antioxidant compound is also briefly discussed.

EXPERIMENTAL

Since we are interested in measuring antioxidant in the insulation of actual high-voltage cables, we analyzed commercially available low-density PE and XLPE resins containing the usual amounts of additives used for cable applications. In fact, these resins are the most commonly used by North American cable manufacturers. The resin manufacturer supplied us with the additive-free base PE resin. Films about 1 mm thick were press-molded at ~ 120°C for ~ 15 minutes. XLPE resin contained ~ 1.5% by weight of dicumyl peroxide as crosslinking agent. Crosslinking was done by heating the films at constant rate (~ 5°C/min) up to 190°C where they were maintained for 5 minutes. PE and XLPE films thus formed were pressed together at ~ 120°C for 5 min to give plates ~ 1 cm thick. These plates were used for oxidation experiments to be described in detail in a subsequent paper. Samples ~ 100 to 200 μm thick were cut with a microtome from the surface of the plates for UV and FTIR measurements. Samples weighing between 0.5 and 1 g were cut from the plates with great care for NAA measurements. NAA results obtained with smaller samples give very disputable results because of the statistical incertitudes induced by the small number of emitted γ-rays.

The NAA measurements were performed at the Slowpoke reactor facility of École Polytechnique de Montréal. Irradiation and counting times were chosen according to standard NAA procedures. The typical error on sulfur contents measured by NAA is ± 25 ppm. UV measurements were performed with a Philips Model PU-88 UV spectrophotometer. FTIR measurements were made at a resolution of 4 cm^{-1} using a Nicolet Model 170 SX spectrometer with a mercury cadmium telluride detector; results presented here correspond to an accumulation of 128 scans. The wavenumber precision of the instrument is ± 0.01 cm^{-1}. The relative lack of sensitivity of IR spectroscopy does not allow an easy detection of the relatively weak antioxidant absorbance bands in the PE spectrum. An improvement is to reduce the intensity of interference fringes by using a polarizer and placing the sample at PE's

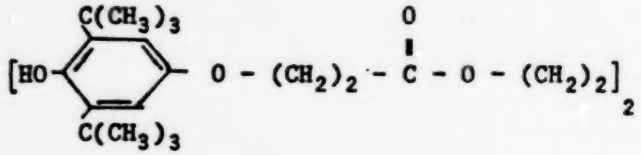
Brewster angle (~ 57°).[9] Reference spectra of the pure additives suspected to be present in the resins were recorded with a diffuse reflectance accessory.

UV MEASUREMENTS

The UV spectrum in the 200-350 nm range of PE with the antioxidant compound is shown in Fig. 1. The broad band at ~ 270-290 nm is assigned to phenyl groups, which are present in most antioxidant systems.[2] We have observed that press-molding above 120°C leads to loss of some antioxidant (i.e. phenyl groups). Samples stored at 22°C for many months also lose some antioxidant by diffusion, as it is well-known.[1,10]

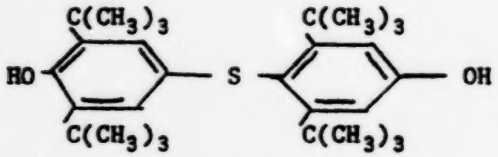
In order to tentatively identify the antioxidant contained in our samples, we recorded the spectra of various antioxidants

- Irganox 1035^{R} (Ciba-Geigy Trade Mark of 2,2' Thiodiethyl-bis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate])



(MW = 744)

- Santonox^{R} (Monsanto Trade Mark for 4,4' Thiobis (3-methyl-6-t-butyl phenol)).



(MW = 359)

and antioxidant synergists

- DSTDP (distearyl thiodipropionate)

$[CH_3(CH_2)_{17}\ OOC(CH_2)_2]_2\ S$ (MW = 683)

and DLTDP (dilauryl thiodipropionate)

$[(C_{12}H_{25})\ OOC(CH_2)_2]_2\ S$ (MW = 514)

These additives were selected because they all contain sulfur which is known to be present in relatively large concentration in the resins studied.[8] An interesting result shown in Fig. 2 is that the synergists (DSTDP and DLTDP) do not absorb UV in the 270-280 nm range where the phenyl groups of Irganox 1035 and Santonox absorb strongly. The strong absorbance in the 220-230 nm range is due to double bonds and in a PE sample they cannot be easily distinguished from the normal absorbance of the polymer. Thus, for all practical purposes, UV spectroscopy is useful only to detect the phenyl groups of the antioxidant. In other words, the results of Fig. 1 show that the PE samples studied contain an antioxidant but nothing can be said about the presence or absence of a synergist. As Santonox is not used anymore in cable insulations since ~ 1975 when it was shown that it migrates very rapidly out of PE,[1] the most likely antioxidant detected in our samples by UV is Irganox 1035.

FTIR MEASUREMENTS

Figure 3 shows the diffuse reflectance IR spectra of the pure compounds Irganox 1035 and the thioesters (DLTDP and DSTDP). The peak positions used for the identification of the additives are those at (i) 1742, 1161, 1233 cm^{-1} for thioesters and (ii) 1736, 1140, 1200 cm^{-1} for Irganox 1035, in the order of their intensities. The difficulties involved in their exact identification are: (i) the major absorbance bands for these additives fall in the same spectral range; (ii) the ester absorption is close to that of the major oxidation by-products of PE. The latter is even more evident in XLPE whose antioxidant ester group content is greatly reduced by crosslinking. Also it is impossible to make a distinction between thioesters. Thus, it could be difficult to estimate the antioxidant content, especially in XLPE and aged PE, from the ester absorbance bands. It is therefore recommended to verify the presence of secondary absorbance bands that do not overlap with those of PE or other additive bands.

In order to determine whether the absorbance peak at 1742 cm^{-1} observed in the spectrum of the cable PE sample containing the standard amount of antioxidant compound for cable application (Fig. 4) is due to Irganox 1035 or to synergist (or to both), we prepared samples with 1500 ppm of Irganox 1035 and with 3000 ppm of DSTDP. Their spectra, in the regions 1760-1680 cm^{-1} and 1280-1100 cm^{-1} are shown in Figs. 4 and 5, respectively. The sample with 1500 ppm of Irganox 1035 absorbs at 1736 cm^{-1} which corresponds to a shoulder in the PE cable resin (Fig. 4). Since Irganox 1035 has been detected by UV spectroscopy, it should be concluded that this shoulder at 1736 cm^{-1} has to be assigned to this antioxidant. It should be noted that none of the absorbance bands of Santonox were observed in the FTIR spectrum of the PE cable resin, which supports our contention that the antioxidant used is Irganox 1035. The absorbance maximum at 1742 cm^{-1} in the PE cable resin corresponds to the maximum absorbance of the sample of PE + 3000 ppm of DSTDP. That indeed this synergist is present in the PE cable resin is confirmed by the major absorbance bands in the region 1280-1100 cm^{-1} (Fig. 5). DSTDP and DLTDP having nearly identical IR spectra (Fig. 3),

this implies that FTIR spectroscopy cannot distinguish one from the other. Whatever its exact nature (DSTDP or DLTDP), the presence of an antioxidant synergist in the PE resin studied is confirmed.

The FTIR spectrum of XLPE is somewhat different since the absorbance of the ester band at 1742 cm^{-1} has been significantly reduced and three important shoulders are visible at ~ 1724, 1710 and 1691 cm^{-1} (Fig. 6). The bands at 1724 and 1710 cm^{-1} are assigned to ketones and carboxylic acid, respectively, which are oxidation by-products induced by the high temperature during crosslinking. The 1691 cm^{-1} band is due to acetophenone, a crosslinking by-product. The bands at 1161 and 1233 cm^{-1} assigned to DSTDP also have a smaller absorbance in XLPE (Fig. 7) than in PE. On the other hand, the absorbance of the bands of Irganox 1035 at ~ 1140, 1200 and 1260 cm^{-1} is not very much changed (compare Figs. 7 and 5). These results suggest that during crosslinking some of the synergist molecules have been consumed or, at least, broken down by the high temperature and/or by a chemical reaction with dicumyl peroxide.[12] The remaining part of the antioxidant compound could then be grafted to PE chains which would explain why it cannot be easily extracted from XLPE.[7,8] The sulfur content measurements are in agreement with that suggestion.

The approximate content of antioxidant and of synergist can be estimated from a comparison of the absorbance bands of the samples with various known amounts of Irganox 1035 and DSTDP. However, it should be noted that the absorbance maximum of the PE cable resin in Fig. 4 is the sum of two overlapping bands, at 1742 and 1736 cm^{-1}. Therefore, it is very difficult to make a precise evaluation of the antioxidant and of the synergist by a direct comparison of the ester band absorbance. Nevertheless, a first approximation was attempted and the results given in Table 1 suggest that the PE resin with the antioxidant compound contains less than 3000 ppm of DSTDP (from the absorbance of the 1161, 1233 and 1742 cm^{-1} bands) and more than 1500 ppm of Irganox 1035 (from the band at 1736 cm^{-1}). An approximately equal amount of ~ 2500 ppm for both additives seems a reasonable estimation from the FTIR results shown in Table 1.

NAA MEASUREMENTS

Both Irganox 1035 and DSTDP (or DLTDP) contain sulfur that can be detected by NAA.[3] The sulfur content thus determined is 220 ± 25 ppm in PE and 210 ± 25 ppm in XLPE. Additive-free PE does not contain more than ~ 10-20 ppm of sulfur, which is the detection limit of NAA for that element. The difference observed between PE and XLPE is small and within experimental error; at most, it represents less than 10% of the original content. This small sulfur content difference in XLPE is in contrast with the more important reduction in the ester group content, as determined by FTIR spectroscopy. It must be concluded that some antioxidant compound molecules have been broken down during crosslinking. If we assume that some of them have been grafted to the polymer's chains, this would mean that part of the sulfur is also grafted and thus unfunctional, especially as a hydroperoxide decomposer - the major function of sulfur in antioxidants. This is in agreement with the fact that XLPE has a much shorter oxidation induction time than PE as will be discussed in detail in a subsequent paper.

If Irganox 1035 were the only sulfur-containing additive in our PE samples, the measured 220 ppm would correspond to ~ 5000 ppm of Irganox 1035. This is a very high and unrealistic value for antioxidant concentration. The sample with 3000 ppm of DSTDP contains 120 ± 25 ppm of sulfur, which is in excellent agreement with the 140 ppm predicted from the molecular weight ratio of sulfur and DSTDP. A synergist content of 2500 ppm (as predicted by FTIR measurements) would mean ~ 110 ppm of sulfur in PE, which implies that Irganox 1035 would also contribute ~ 110 ppm of sulfur. Thus, the sulfur-content measurements by NAA confirm the FTIR results and they can help identify and evaluate the content of the antioxidant compound used in many cable applications.

CONCLUSIONS

It has been shown that a combination of UV and FTIR spectroscopy and NAA (or any other technique measuring sulfur) measurements allows the identification of the two components of the antioxidant compound used in PE resin for cable applications. In fact, the combination of FTIR and NAA results is the only reliable way to evaluate the antioxidant-compound content in XLPE. Note that this cannot be achieved by a single technique since UV spectroscopy is useless with XLPE and cannot easily identify synergists; FTIR spectroscopy can identify the antioxidant components in unaged PE but this is much more difficult in aged PE and in XLPE; the sulfur content in XLPE does not give directly the fraction of functional (i.e. ungrafted) antioxidant compound.

FTIR spectroscopy and NAA measurements reveal that the studied PE and XLPE samples contain identical (~ 2500 ppm) antioxidant (Irganox 1035) and synergist (DSTDP or DLTDP) contents. A detailed study of oxidation and antioxidation kinetics in PE and XLPE will be given in a subsequent publication.

ACKNOWLEDGMENTS

We are greatly indebted to R.M. Eichhorn and R. Turbett for many stimulating suggestions and comments. We are also grateful to G. Kennedy of École Polytechnique de Montréal who performed the NAA measurements.

Table 1

Ratio of IR absorbance over sample thickness (A/L) for various bands of antioxidant and synergist

Sample Identification	1742 cm^{-1}	1736 cm^{-1}	1233 cm^{-1}	1161 cm^{-1}
PE + antioxidant compound	3.92	- 2.6	0.45	2.60
PE + 3000 ppm DSTDP	4.80	- 3	0.66	2.55
PE + 1500 ppm Irganox 1035	?	1.5	-	-
XLPE + antioxidant compound	2.30	?	0.27	1.20

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FIGURE CAPTIONS

Figure 1: UV absorbance spectrum of PE sample containing unknown amount of antioxidant compound used for cables.

Figure 2: UV absorbance spectra of antioxidants (Irganox 1035 and Santonox) and antioxidant synergists (DSTDP and DLTDP).

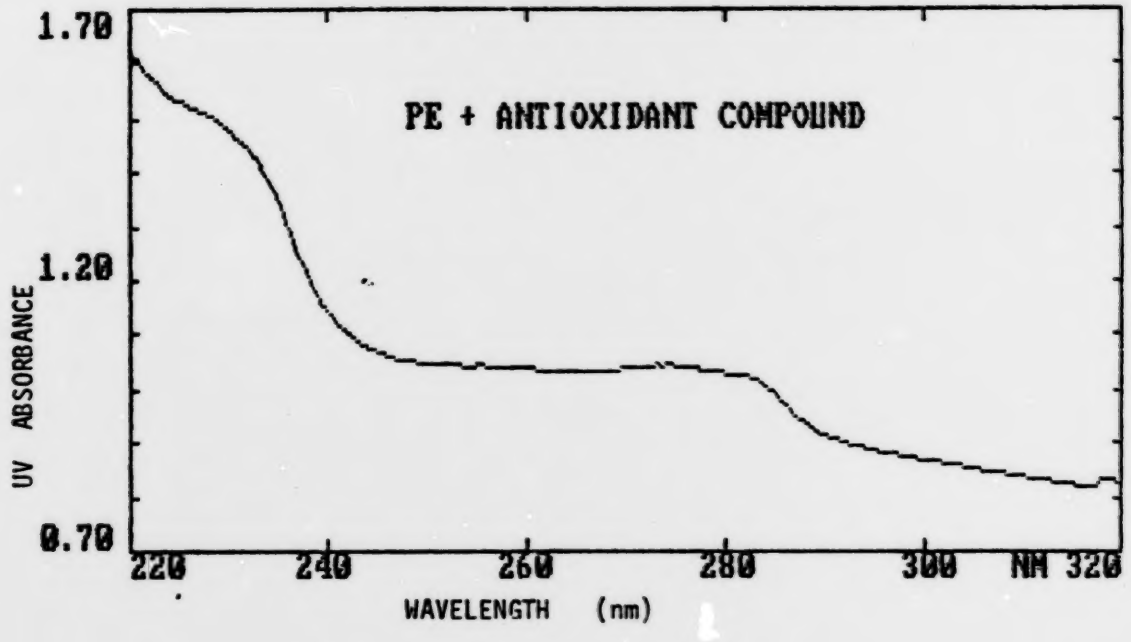
Figure 3: FTIR spectrum of Irganox 1035 and of DSTDP obtained by diffuse reflectance on a mixture with Kbr.

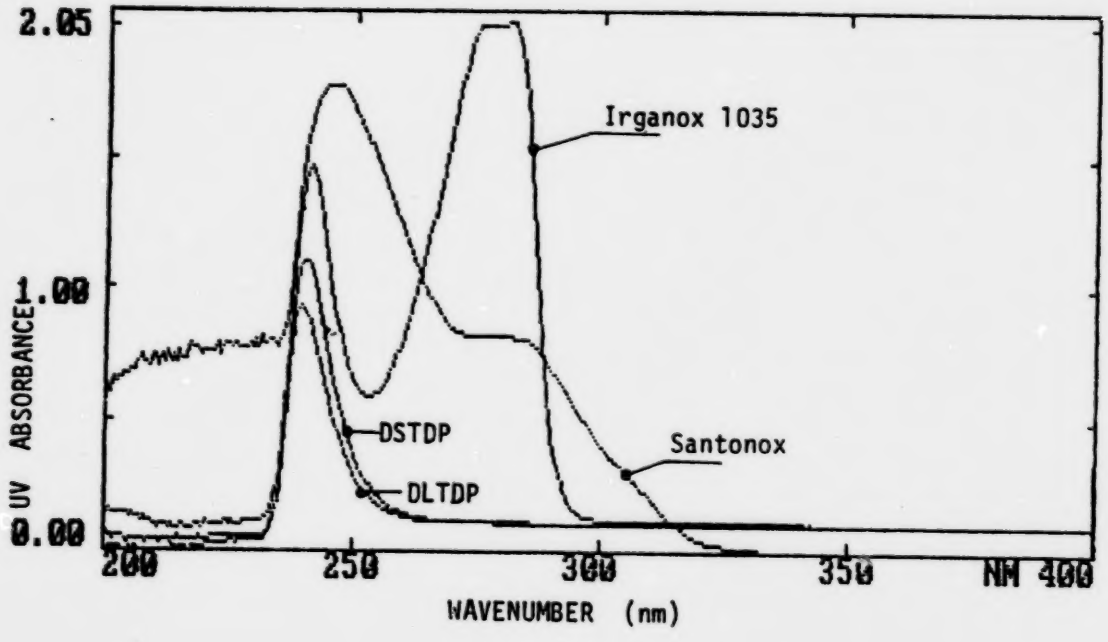
Figure 4: FTIR absorbance spectrum of various PE samples in the 1680 to 1760 cm^{-1} region.

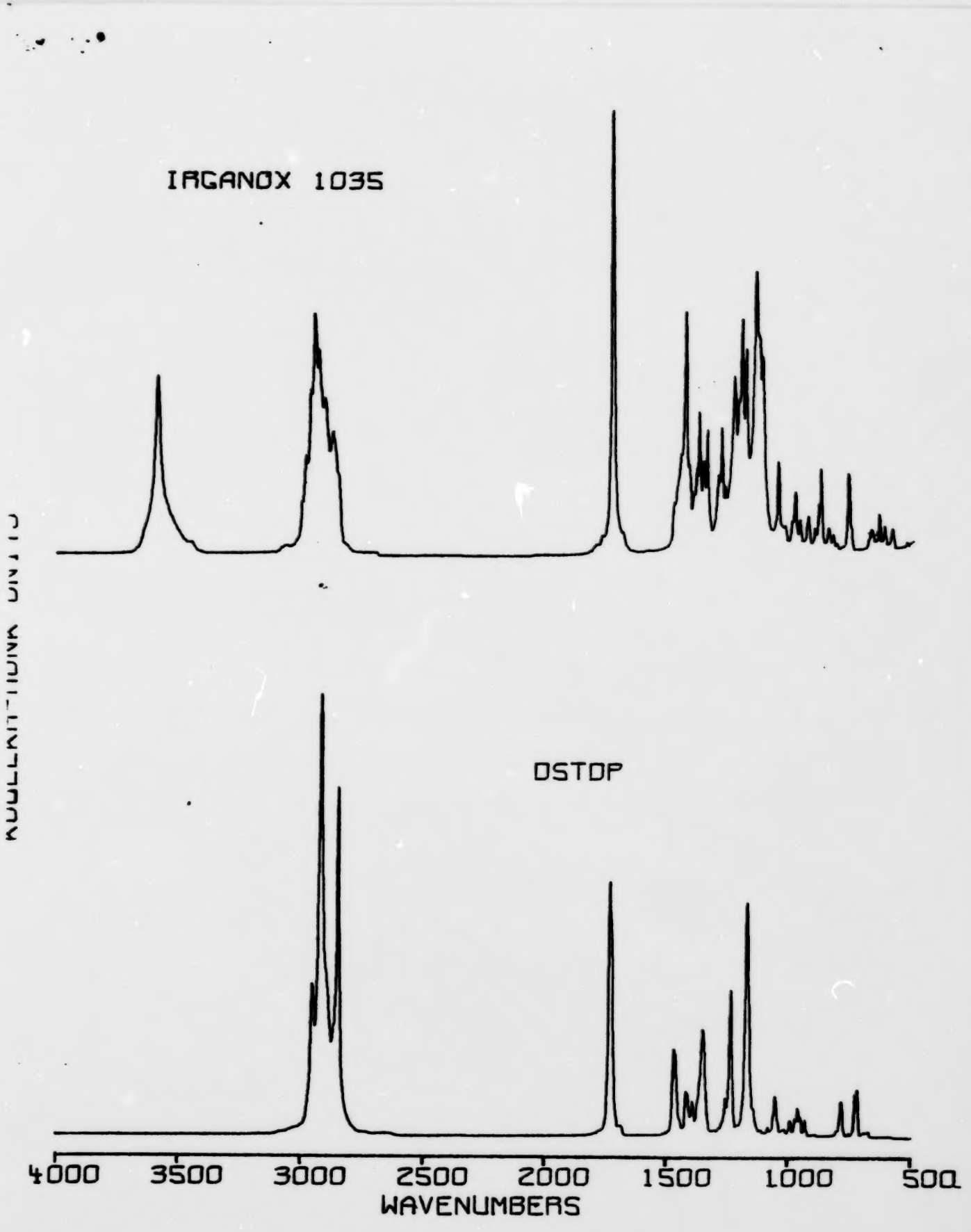
Figure 5: FTIR absorbance spectrum of various PE samples in the 1100 to 1280 cm^{-1} region.

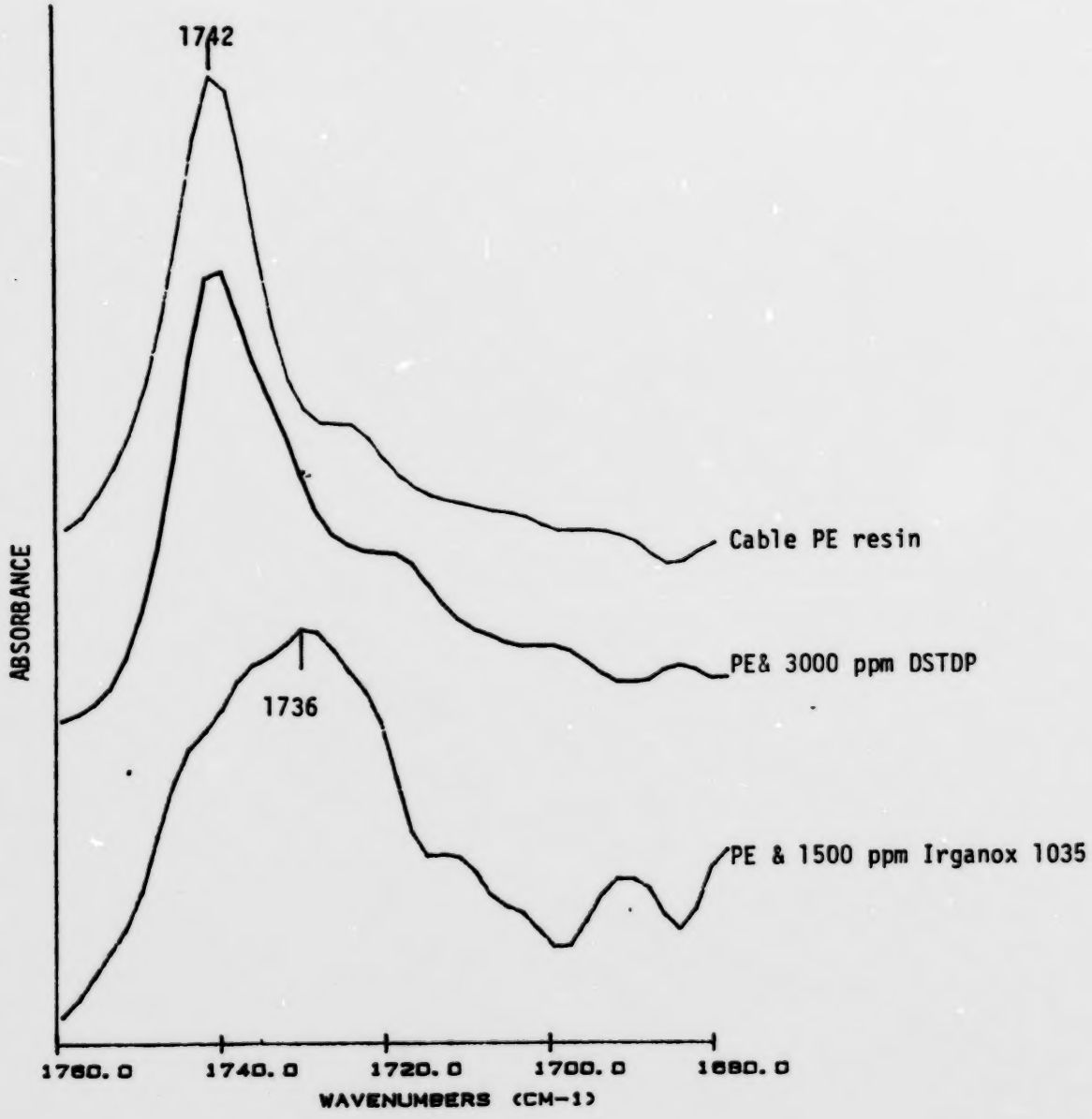
Figure 6: FTIR absorbance spectrum of cable XLPE in the region 1680 to 1760 cm^{-1}.

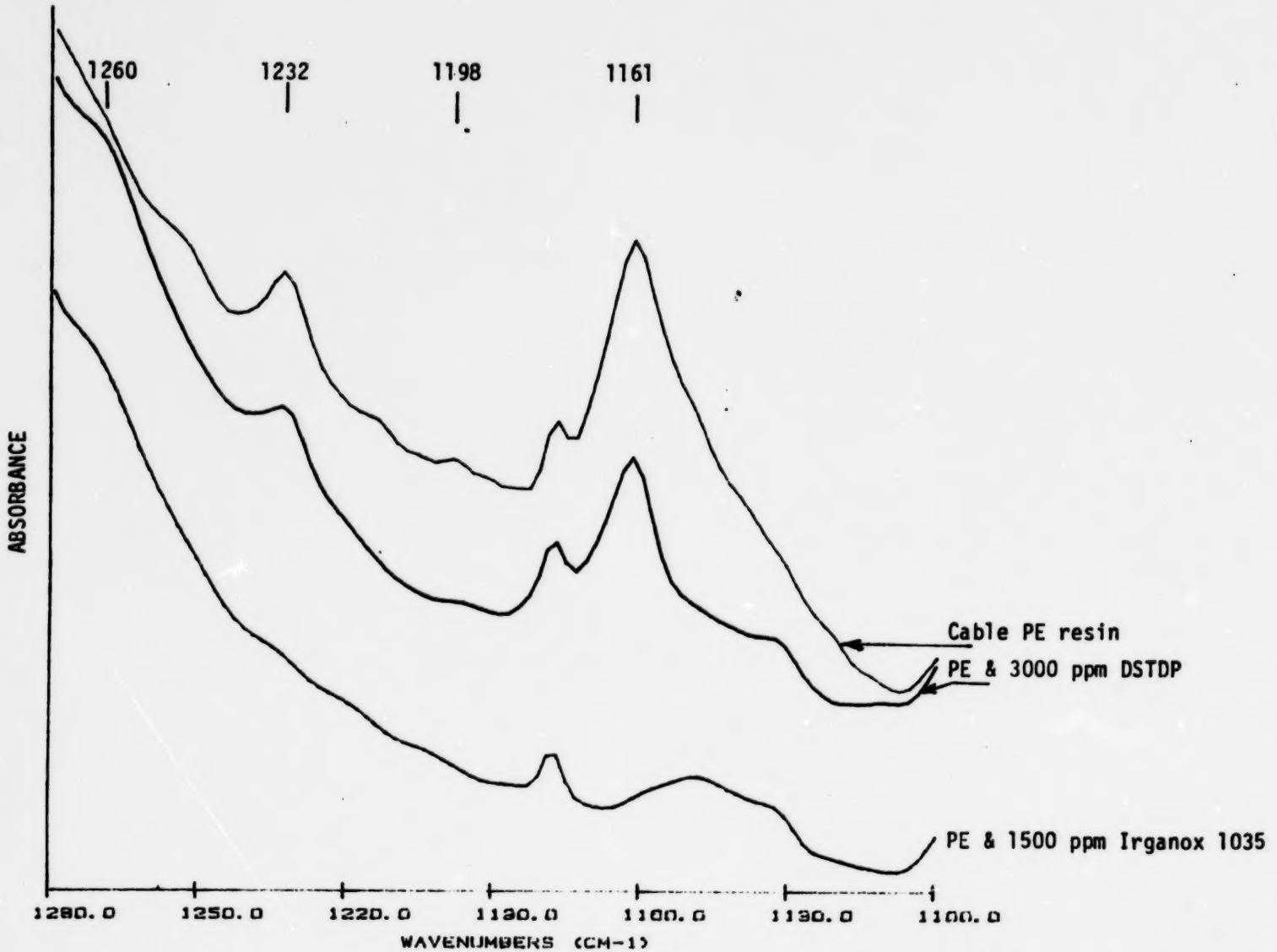
Figure 7: FTIR absorbance spectrum of cable XLPE in the region 1100 to 1280 cm^{-1}.

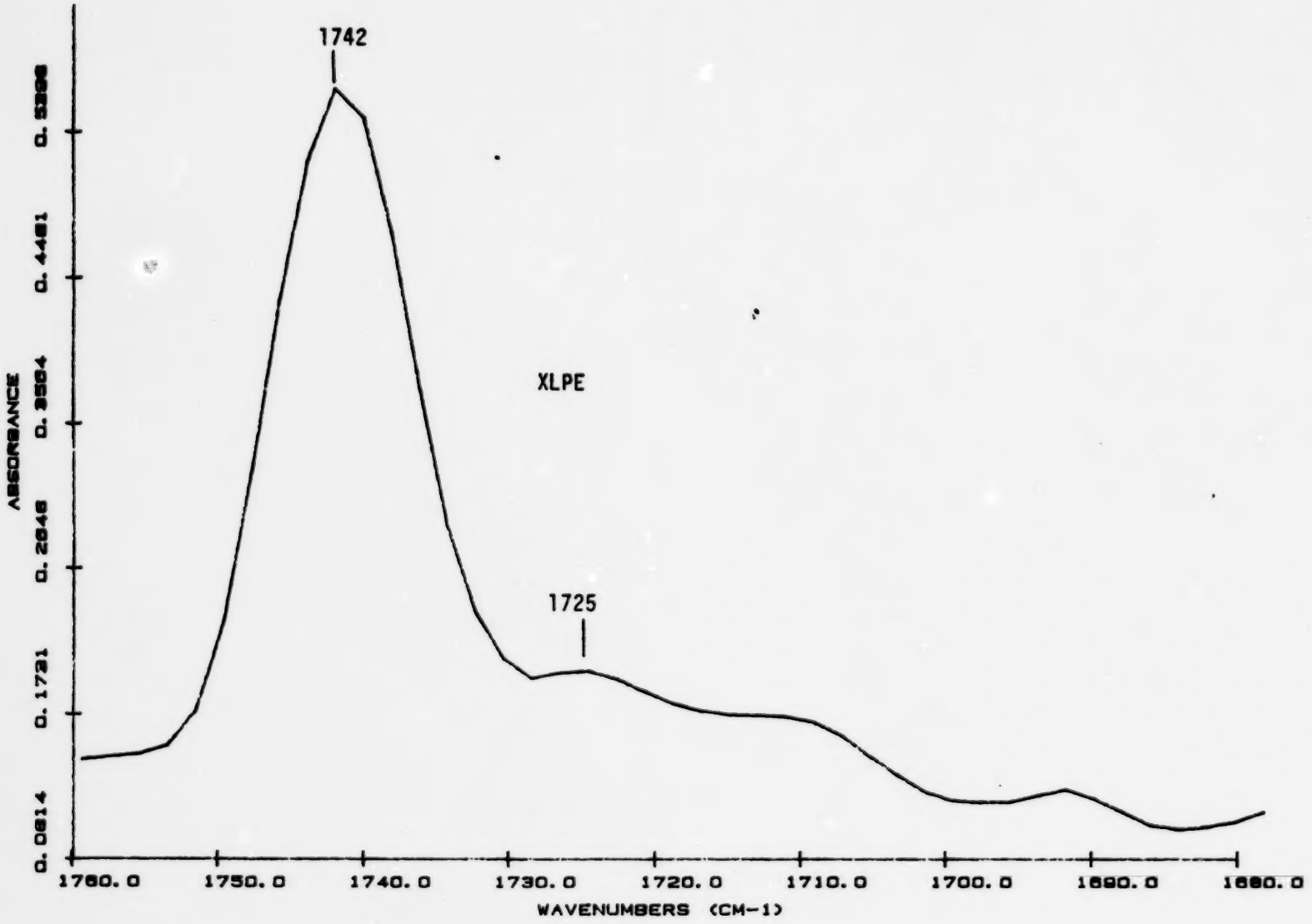

PE + ANTIOXIDANT COMPOUND
1.70
1.20
0.70
UV ABSORBANCE
220
240
260
280
300
NM 320
WAVELENGTH (nm)


2.05
1.00
0.00
UV ABSORBANCE
Irganox 1035
DSTDP
DLTDP
Santonox
200
250
300
350
NM 400
WAVENUMBER (nm)


IRGANOX 1035
DSTDP
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBERS


1742
1736
Cable PE resin
PE& 3000 ppm DSTDP
PE & 1500 ppm Irganox 1035
ABSORBANCE
1760.0
1740.0
1720.0
1700.0
1680.0
WAVENUMBERS (CM-1)


1260
1232
1198
1161
ABSORBANCE
Cable PE resin
PE & 3000 ppm DSTDP
PE & 1500 ppm Irganox 1035
1280.0
1250.0
1220.0
1190.0
1160.0
1130.0
1100.0
WAVENUMBERS (CM-1)


1742
1725
XLPE
ABSORBANCE
0.0814
0.1731
0.2648
0.3564
0.4481
0.5398
1760.0
1750.0
1740.0
1730.0
1720.0
1710.0
1700.0
1690.0
1680.0
WAVENUMBERS (CM-1)

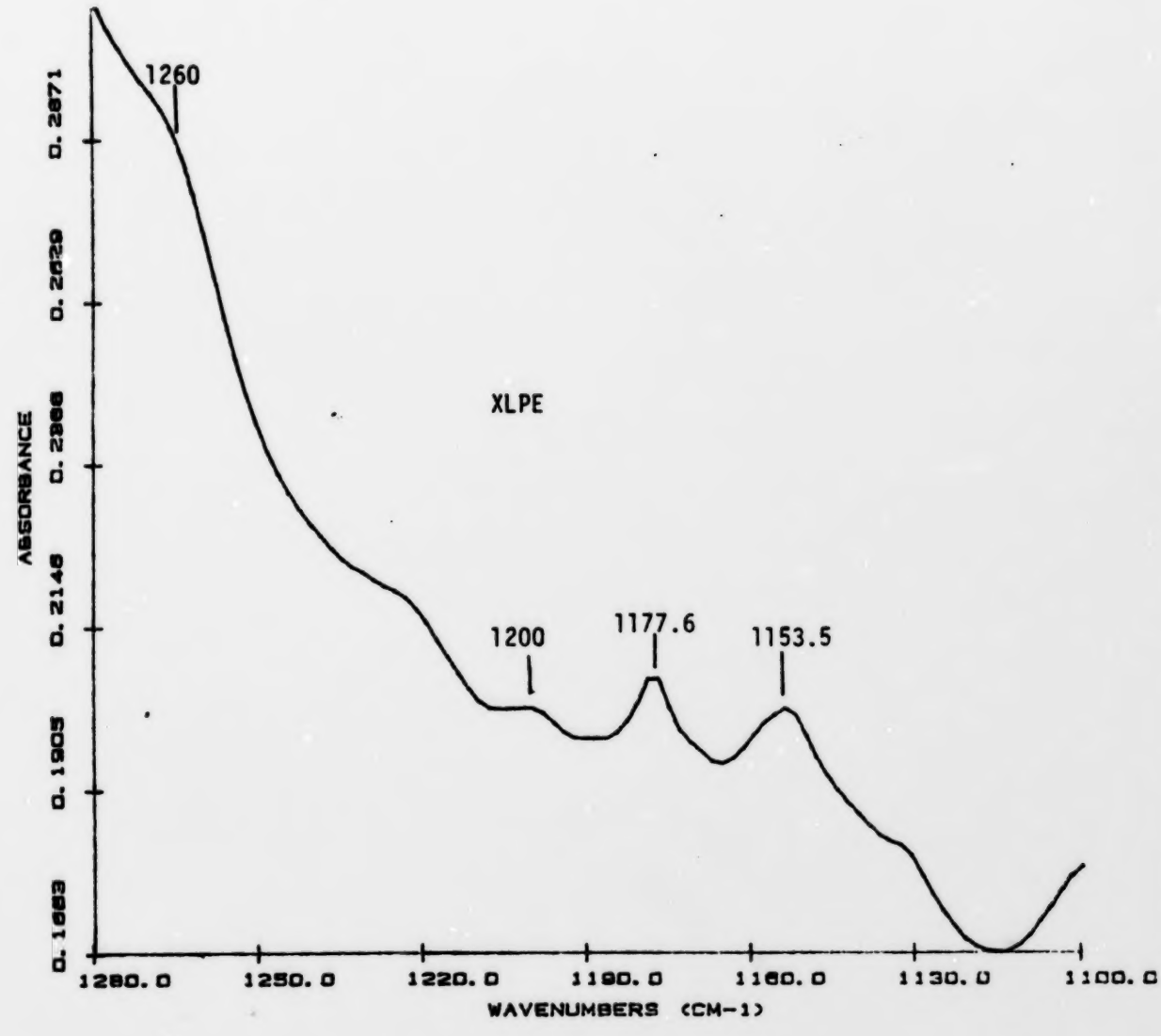

1260
XLPE
1200
1177.6
1153.5
ABSORBANCE
0.2871
0.2629
0.2388
0.2146
0.1905
0.1663
1280.0
1250.0
1220.0
1190.0
1160.0
1130.0
1100.0
WAVENUMBERS (CM-1)

Fig. 7